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LOW-ENERGY INTERACTION OF METAL CLUSTER IONS WITH SURFACES

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Ion-beam treatment of materials is one of the widely applied methods for a number of research and industrial purposes. Along with traditional monatomic species, atomic or molecular clusters (aggregates of atoms or molecules) have attracted significant attention during the last two decades [1-3]. One of advantages of cluster beam technique is in possibility to control cluster sizes from a few up to many thousands of constituents. This paves a way for investigation of fundamental physical aspects of the transition from the atomic scale to bulk material [4]. On the other hand, finite size effects in supported (deposited) clusters, which are often called nanoparticles (NP), lead to specific properties providing a significant impact over a range of fields such as electronics and optics, biology and medicine, catalysis and other nanotechnology-related branches [1, 5-8]. Increase of cluster kinetic energy provides a possibility to apply this technique for shallow doping, sputtering and polishing [2, 3, 8, 9]. In the recent years, clusters of inert gases and fullerenes have become a powerful tool in secondary ion mass spectrometry [10].

In this paper, however, we would like to focus on the low-energy deposition of metal clusters, so-called soft landing. In this regime, the kinetic energy per cluster atom or molecule should be much below the binding (cohesive) energy of the cluster constituents. The soft landing does not lead to cluster fragmentation, i.e. the cluster preserves its composition. However, the shape can be slightly distorted compared to that in the gas phase due to the physisorption and formation of van der Waals bonds with surface atoms (see schematic picture in Fig. 1). Study of soft landed clusters is driven by the efforts to utilise the above-mentioned unique properties of supported metal NPs for applications. A number of studies were carried out and it was shown that surface diffusion of clusters must be considered [11]. Since the activation barrier strongly depends on the cluster-surface bonding, cluster mobility is favored on weakly interacting materials, such as graphite or amorphous carbon. If the lattice mismatch between the cluster and the substrate is significant, vibrational coupling between these can overcome the small energy barrier of the surface potential, thus, leading to Brownian-like motion of the cluster [12]. Particles moving on the surface can meet and interact yielding two main possible scenarios: coalescence and agglomeration. Coalescence leads to merging of two (or more) clusters and the formation of a single larger particle with

potentially different shape. This is preferable regime for small clusters. In the case of metal clusters consisting of hundreds or thousands of atoms the tendency is to agglomerate and form islands [12, 13]. Clusters are also tended to be immobilized at natural defect on the surfaces. One of the very well-known phenomena is collection of NPs at step edges of graphite [14].

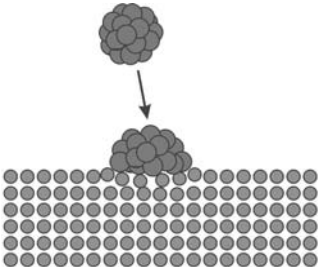

Fig. 1. Schematic picture of cluster deposition.

Despite of a significant number of publications on cluster soft-landing many fundamental physical questions still have to be answered. In the current work we study soft-landing of size-selected silver clusters on a few different substrates to resolve some issues related to surface arrangement of clusters which are of practical importance for a number of applications.

In the experiments, magnetron sputtering cluster apparatus (MaSCA) shown in Fig. 2 is used. The setup consists of several vacuum chambers. For cluster production a commercial source, NC200U from Oxford Applied Research, is connected to the source chamber. In the source, target material is sputtered into an aggregation region where clusters are formed and then expanded into the source chamber. More details about the process of magnetron sputtering can be found elsewhere [15]. Thereafter, the clusters are collimated into a beam by a skimmer. After the skimmer, the cluster beam enters the ion optics. By Einzel lens and two pairs of deflectors the beam parameters are adjusted to enter the electrostatic quadrupole mass selector (EQMS) where clusters are size selected. EQMS consists of four equally distance hyperbolic electrodes surrounded by a grounded shield. These electrodes are divided into two pairs which can be biased (U_{QP}) with opposite polarity, thus, bending the beam of charged clusters of desire masses for 90^{o} into the deposition chamber. For details of the procedure see [15]. To measure intensity of the beam, Faraday cups are used. All chambers are evacuated by turbomolecular pumps (from 230 to 1250 l/s) backed by rotary vane pumps. Using differential pumping a background pressure of 1.0×10^{-7} mbar is reached in the deposition chamber.

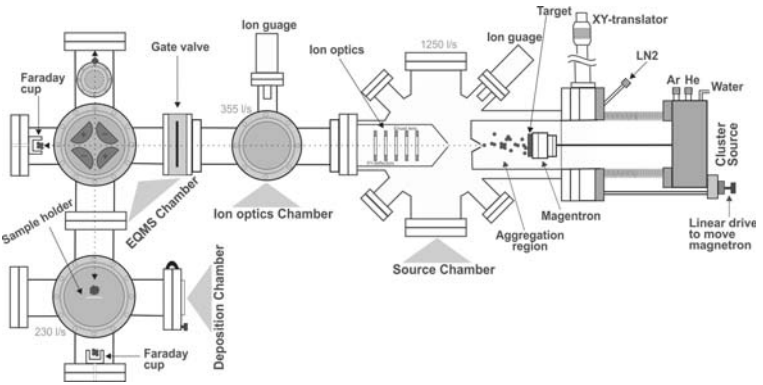

Fig. 2. Schematic drawing of MaSCA.

A silver target of 99.99% purity (from Goodfellow Ltd) is used for cluster production. Size-selected Ag_n clusters are deposited on clean Si(100), highly ordered pyrolytic graphite (HOPG), quartz and quartz spin-coated by 50 nm thick films of polymethylmethacrilate (PMMA) at room temperature. Deposition time is typically varied between 15-30 min to get considerable surface coverage. Cluster kinetic energy is kept in so-called thermal regime providing good conditions for soft-landing from the gas phase where the clusters are assumed to be close to spherical shape. Supported NPs are studied by atomic force microscopy (AFM) in tapping mode using Ntegra Aura nanolaboratory from NT-MDT. Samples with clusters deposited on quartz and PMMA/quartz substrates are also investigated by optical transmittance spectroscopy using Perkin Elmer High Performance Lambda 1050 spectrometer in the interval of wavelengths λ = 300-750 nm.

The clusters inside the source are formed in different sizes from a few up to many thousands of atoms; significant fraction of clusters is ionized. The cluster sizes can be tuned by varying the discharge power, flows of sputtering (Ar) and aggregation (He) gases as well as aggregation length in the source. The size (mass) selection is defined by the geometry of EQMS and to the large extent by voltages applied to the electrodes. Relatively low voltages allow selection of smaller in size (light mass) clusters while with the voltage increase larger (heavier) particles can be selected. Size of the particles is estimated from AFM measurements. Earlier experiments [15] showed that shape of the deposited metal clusters is only slightly deviate from the spherical; the particles became a bit flattened on Si. Thus, the measured height is assumed to be almost equal to NP diameter. In the series of depositions the following EQMS voltages U_{QP} = ±100, ±300, ±500, ±900, ±1400, and ±2000 V are applied.

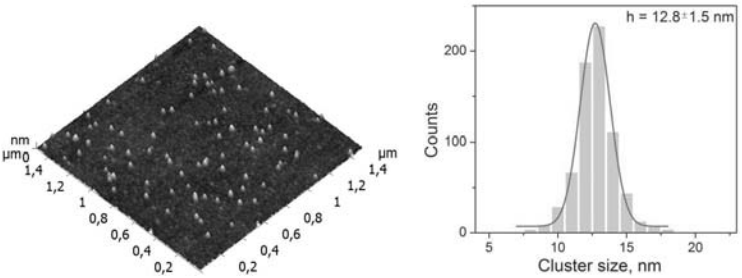

Fig. 3. AFM image of silver clusters on silicon deposited at U_{QP} = ±300 V and histogram of height distribution.

The AFM study shows that the clusters are located on the surface randomly and they do not agglomerate even for coverages close to a monolayer of clusters. This indicates low diffusion mobility of silver clusters on Si at room temperature. An example of AFM image and corresponding height histogram for U_{QP} = ±300 V are shown in Fig. 3. Mean heights and standard deviations for silver clusters deposited in this series of experiments are presented in Fig. 4. The fit curve demonstrates proportionality of cluster size to $\sqrt[3]{U_{QP}}$ which is expected from the theory behind mass selection in EQMS (see for details [15]).

AFM image of clusters deposited on HOPG surface is shown in Fig. 5. Comparison of mean cluster height on HOPG, which is found to be 12.7±1.7 nm, with that on Si, 12.8±1.5 nm, for the same U_{QP} shows very good agreement. This allows concluding that the clusters are soft landed on HOPG without significant shape corrugation. However, one can clearly see

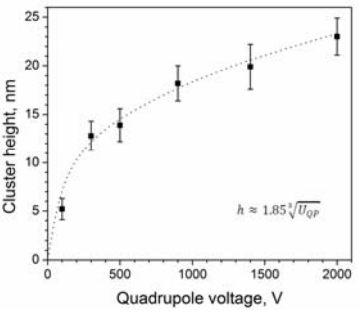

Fig. 4. Mean cluster heights (with standard deviations) for different voltages at EQMS.

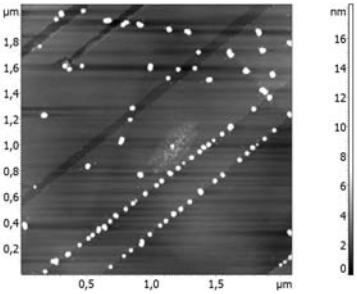

Fig. 5. AFM image of silver clusters deposited on HOPG at U_{QP} = ±300 V.

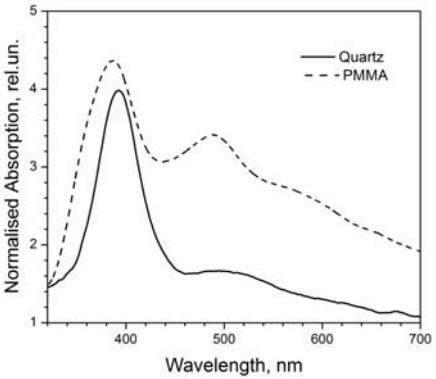

Fig. 6. Normalized optical absorption spectra for bare quartz and quartz coated by PMMA with deposited size-selected (at U_{QP} = ±300 V) silver clusters.

from the AFM image a tendency for clusters to collect at surface defects especially at the steps that is indicated by rows of clusters. In the case of deposition on quartz substrates at U_{QP} = ±300 V mean cluster height is measured to be 12.0±1.9 nm which can be an indication that the clusters are more flattened on quartz compared to Si or HOPG but this issue requires further investigation. The surface location of NPs is random similar to the case of silicon. For the clusters deposited on PMMA mean height is found to be very similar to the case of quartz. The clusters are randomly spread and not making any agglomerates.

The samples with clusters deposited on bare quartz and quartz coated by PMMA (i.e. transparent in visible interval substrates) are also studied using optical spectroscopy. The spectra are shown in Fig. 6. Presence of an absorption band at wavelength $\lambda \approx 400$ nm, which is related to localized surface plasmon resonance (LSPR) on silver NPs [16], can be seen. The other less pronounced band at around 500 nm is most probably related to LSPR of interacting NPs similar to the case described in [17]. Intensity of this band is found to be strongly dependent on cluster surface coverage. With coverage decrease, i.e. increase of interparticle distance, the band has tendency to disappear, thus, supporting our suggestion on the band nature.

Good size selection and possibility to control cluster coverage by tuning the deposition time make the cluster beam technique very attractive towards practical applications. One of the directions can be formation of cluster-based plasmonic systems which are used as optical transducers for biosensors. This possibility has been recently demonstrated for protein detection [18].

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